calculated values[10] of the vicinal coupling constants for the α-configuration are the same reported for compound 6.

(3*S*,4*S*)-3,4-(Isopropylidenedioxy)pentan-1-ol (14). The periodate oxidation of the diol 12 and the subsequent $NaBH_4$ reduction were performed as indicated above for the conversion of 3 into 5. Benzyl alcohol was removed from the reaction mixture by hydrogenolysis to toluene in the presence of 10% Pd/C with H_2 in ethanol at 23 °C and 2 atm. (3*S*,4*S*)-14, as an oil, was obtained in 45% overall yield from 12: $[\alpha]^{20}{}_D$ −14.5° (c 1, $CHCl_3$). When (2*R*,3*R*,6*RS*)-10 was reduced with $NaBH_4$ in isopropyl alcohol, followed by basic treatment, a mixture of 5,6-syn and 5,6-anti diols was obtained. Sequential treatment of the mixture with $HIO_4 \cdot 2H_2O$ and $NaBH_4$ gave (3*R*,4*R*)-14: $[\alpha]^{20}{}_D$ +14.9° (c 1, $CHCl_3$).

Registry No. 1 (isomer 1), 106976-80-1; 1 (isomer 2), 106976-81-2; **2**, 106976-84-5; **3**, 106976-85-6; **3** (diacetate), 106976-86-7; 4, 106976-87-8; **5** (3,5-dinitrobenzoate), 85287-65-6; **6**, 106976-88-9; **7**, 74164-24-2; **8**, 106976-89-0; **9** (5-acetate), 107034-98-0; **10** (racemic isomer 1), 106976-83-4; **10** (racemic isomer 2), 107035-00-7; **10** (2*R*,3*R*,6*R*), 107035-01-8; **10** (2*R*,3*R*,6*S*), 107034-99-1; **10** (2*S*,3*S*,6*R*), 107035-02-9; **10** (2*S*,3*S*,6*S*), 107035-03-0; **11**, 106976-90-3; **12**, 106976-91-4; **13**, 106976-92-5; **14** (3*S*,4*S*), 106987-87-5; **14** (3*R*,4*R*), 106987-88-6; **15**, 106976-93-6; 2-lithio-1,3-dithiane, 36049-90-8; 1,2-(isopropylidenedioxy)-3-bromopropane, 34637-20-2; 3-bromo-1,2-propanediol, 34637-21-3; 2-[2,3-(isopropylidenedioxy)propyl]-1,3-dithiane, 106976-78-7; cinnamaldehyde, 104-55-2; 2-[2,3-(isopropylidenedioxy)propyl]-2-(1-hydroxy-3-phenyl-2-propenyl)-1,3-dithiane (isomer 1), 106976-79-8; 2-[2,3-(isopropylidenedioxy)propyl]-2-(1-hydroxy-3-phenyl-2-propenyl)-1,3-dithiane (isomer 2), 106976-94-7; *trans*-2,2,5-trimethyl-1,3-dioxolane-4-methanol, 81739-14-2; *trans*-4-(bromomethyl)-2,2,5-trimethyl-1,3-dioxolane, 106976-82-3; (4*S*,5*S*)-*trans*-2,2,5-trimethyl-1,3-dioxolane-4-methanol, 85249-45-2; (4*R*,5*S*)-4-(bromomethyl)-2,2,5-trimethyl-1,3-dioxolane, 107034-97-9; 3,5-dinitrobenzoyl chloride, 99-33-2.

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Synthesis and pK_a Values of 4,5-Dinitro-1,8-biphenylenediol[1]

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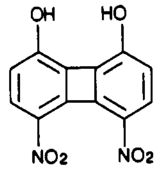
1,8-Biphenylenediol has been shown to use its two hydroxy groups to form hydrogen bonds to the same oxygen atom.[2-4] Because the hydrogen bonding ability of structurally similar acids increases with their increasing acidity[5] more acidic derivatives of 1,8-biphenylenediol are of interest. Since ortho and para nitro substituents are among the strongest electron withdrawers of common substituents and since an ortho nitro substituent could give complications from internal hydrogen bonding, we have prepared 4,5-dinitro-1,8-biphenylenediol (1) and determined its ionization constants.



1

Experimental Section

2,3-Dichloro-4-nitroanisole. A mixture of 8.47 g (48 mmol) of 2,3-dichloroanisole, 7.64 g (58 mmol) of nitronium tetrafluoroborate, and 400 mL of glacial acetic acid was kept at 90–110 °C for 1 h and then stirred at room temperature for 12 h. The reaction mixture was poured into 500 mL of water and extracted with ether. The combined organic layers were washed with water and sodium carbonate solution and dried with magnesium sulfate. Removal of the solvent gave 8.0 g of brownish viscous oil, which was chromatographed with 35:1 petroleum ether–ethyl acetate to give three fractions, of which the last was 1.76 g (17% yield) of 2,3-dichloro-4-nitroanisole: ^{1}H NMR (acetone-d_6, 90 MHz) δ 8.17 (d, J = 9 Hz, 1 H, H-5), 7.32 (d, 1 H, H-6), 4.09 (s, 3 H, OCH_3); mass spectrum, m/z 222 (M^+). An analytical sample was recrystallized three times from hexane to give pale yellow prisms: mp 81–82 °C.

Anal. Calcd for $C_7H_5O_3Cl_2N$: C, 37.87; H, 2.27; Cl, 31.94; N, 6.31. Found: C, 38.05; H, 2.33; Cl, 31.62; N, 6.23.

2,3-Dichloro-6-nitroanisole and 2,3-Dichloro-4,6-dinitroanisole. The first fraction in the chromatography just described was 0.4 g of a mixture of starting 2,3-dichloroanisole and 2,3-dichloro-6-nitroanisole: ^{1}H NMR (acetone-d_6, 90 MHz) δ 7.90 (d, J = 9 Hz, 1 H, H-5), 7.59 (d, 1 H, H-4), 4.05 (s, 3 H, OCH_3): mass spectrum, m/z 222 (M^+).

The second fraction was 0.3 g (2% yield) of 2,3-dichloro-4,6-dinitroanisole: ^{1}H NMR (acetone-d_6, 90 MHz) δ 8.65 (s, 1 H, H-5), 4.13 (s, 3 H, OCH_3).

2,2′-Diiodo-6,6′-dimethoxy-3,3′-dinitrobiphenyl (3). A mixture of 10.5 g (22.5 mmol) of 2,2′-diiodo-6,6′-dimethoxybiphenyl (2), 17.95 g (135 mmol) of nitronium tetrafluoroborate, and 265 mL of glacial acetic acid was refluxed for 1.2 h. The cooled mixture was poured into 500 mL of water and extracted with ether. The combined organic layers were washed with 150 mL of water, sodium carbonate solution, sodium bisulfite solution, and water and then dried with magnesium sulfate. Evaporation of the solvent gave 12.4 g of reddish solid that was chromatographed on silica gel with 3:1 hexane–ethyl acetate to give 4.49 g (8.08 mmol, 36%) of yellow crystalline 3. Three recrystallizations from chloroform–hexane gave crystals: mp 202.5–203 °C; R_f 0.32 (2:1 hexane–ethyl acetate); IR (KBr) 1565, 1340 (NO_2) cm^{-1}; ^{1}H NMR (acetone-d_6, 90 MHz) δ 8.09 (d, J = 9 Hz, 2 H, H-4,4′), 7.37 (d, 2 H, H-5,5′), 3.81 (s, 6 H, OCH_3); mass spectrum, m/z 556 (M^+).

Anal. Calcd for $C_{14}H_{10}O_6N_2I_2$: C, 30.24; H, 1.81; N, 5.04; I, 45.64. Found: C, 30.45; H, 1.94, N, 4.88; I, 45.06.

2,2′-Diiodo-6,6′-dimethoxy-3-nitrobiphenyl, 2,2′-Diiodo-6,6′-dimethoxy-5-nitrobiphenyl, 2,2′-Diiodo-6,6′-dimethoxy-3,5′-dinitrobiphenyl, and 2,2′-Diiodo-6,6′-dimethoxy-3,3′,5,5′-tetranitrobiphenyl. Other products from the preceding reaction were obtained by column and/or preparative thin layer chromatography and identified from the following evidence. All the R_f values are in 2:1 hexane–ethyl acetate.

A 7% yield (0.83 g) of 2,2′-diiodo-6,6′-dimethoxy-3-nitrobiphenyl: R_f 0.52; ^{1}H NMR (acetone-d_6, 90 MHz) δ 8.03 (d, J = 9 Hz, 1 H, H-4), 7.67–7.46 (dd, $J_{3',4'}$ = 6 Hz, $J_{3',5'}$ = 3 Hz, 1 H, H-3′), 7.38–7.18 (m, 3 H, H-4′, H-5, H-5′), 3.86 (s, 3 H, OCH_3), 3.75 (s, 3 H, OCH_3); mass spectrum, m/z 511 (M^+), 384 (M^+ − I).

A 4% yield (0.5 g) of 2,2′-diiodo-6,6′-dimethoxy-5-nitrobiphenyl: R_f 0.70; ^{1}H NMR (acetone-d_6, 90 MHz) δ 8.01 (d, J = 9 Hz, 1 H, H-4), 7.75–7.15 (m, 4 H, H-3, H-3′, H-4′, H-5′), 3.80 (s, 3 H, OCH_3), 3.59 (s, 3 H, OCH_3); mass spectrum, m/z 511 (M^+).

A 32% yield (4.0 g) of 2,2′-diiodo-6,6′-dimethoxy-3,5′-dinitrobiphenyl: R_f 0.47; ^{1}H NMR (acetone-d_6, 90 MHz) δ 8.19–8.00 (m, 2 H, H-4, H-4′), 7.78 (d, J = 9 Hz, 1 H, H-3′), 7.45 (d, J = 9 Hz, 1 H, H-5), 3.95 (s, 3 H, OCH_3), 3.62 (s, 3 H, OCH_3); mass spectrum, m/z 556 (M^+), 429 (M^+ − I).

A trace of 2,2′-diiodo-6,6′-dimethoxy-3,3′,5,5′-tetranitrobiphenyl: R_f 0.67; ^{1}H NMR (acetone-d_6, 90 MHz) δ 8.65 (s, 2 H, H-4,4′), 3.80 (s, 6 H, OCH_3); mass spectrum, m/z 519 (M^+ − I).

1,8-Dimethoxy-4,5-dinitrobiphenylene (4). A solution of 500 mg (0.90 mmol) of 3 in 50 mL of dry dimethylformamide was

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[1] This investigation was supported in part by Grant No. CHE-8114770 from the National Science Foundation. Abstracted in part from the Ph.D. Dissertation of K. Ahn, The Ohio State University, 1986.

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refluxed under argon for 10 min and then 0.7 g of activated copper bronze[6] was added in one portion. After the mixture was refluxed for 8 h, the cooled solution was poured into 75 mL of water at 0 °C and filtered. The collected solid was extracted in a Soxhlet extractor for 26 h with methylene chloride. Evaporation of the solvent left 294 mg of yellowish orange solid, which was chromatographed on silica gel with 4:1 petroleum ether–ethyl acetate to give 214 mg (0.71 mmol, 79% yield) of 4. An analytical sample was recrystallized three times from chloroform–hexane to give orange needles: mp 246–247 °C; ^{1}H NMR (CDCl$_3$, 90 MHz, ~55 °C) δ 7.3 (d, J = 9 Hz, 2 H, H-3,6), 6.68 (d, 2 H, H-2,7), 3.95 (s, 6 H, OCH$_3$); mass spectrum, m/z 302 (M$^+$).

Anal. Calcd for $C_{14}H_{10}O_6N_2$: C, 55.64; H, 3.33; N, 9.27. Found: C, 55.41; H, 3.41; N, 9.07.

The use of cuprous oxide at 270 °C for 5 min also gave 4, but in only 28% yield.

6,6′-Diiodo-2,2′-biphenyldiol (5). A solution of 14.4 mL of 1 M boron tribromide in n-hexane was added to 6.68 g (3.61 mmol) of 2,2′-diiodo-6,6′-dimethoxybiphenyl[7,8] in 35 mL of dry benzene at 65–70 °C under argon. After 19 h of reflux the solution was cooled in an ice bath and ice water added dropwise. Extraction, first with ether and then with methylene chloride, gave a combined extract that was washed with water and dried over magnesium sulfate. Evaporation of the solvent gave an almost quantitative yield of while solid 5: R_f 0.5 (1:1 hexane–ethyl acetate). An analytical sample was recrystallized twice from chloroform–hexane to give white needles: mp 198–200 °C; IR (KBr) 3540–3200 (OH) cm^{-1}; ^{1}H NMR (acetone-d_6, 90 MHz) δ 7.70–7.44 (dd, $J_{4,5}$ = 9 Hz, $J_{3,5}$ = 6 Hz, 2 H, H-5,5′), 7.12–6.97 (m, 4 H, H-3,3′, H-4,4′); mass spectrum, m/z 438 (M$^+$).

Anal. Calcd for $C_{12}H_8O_2I_2$: C, 32.91; H, 1.84; I, 57.95. Found: C, 33.00; H, 1.94; I, 57.46.

6,6′-Diiodo-5,5-dinitro-2,2′-biphenyldiol (6) and 6,6′-Diiodo-3,5′-dinitro-2,2′-biphenyldiol. A mixture of 3.83 g (8.74 mmol) of 5, 3.48 g (26.2 mmol) of nitronium tetrafluoroborate, and 110 mL of glacial acetic acid was stirred at room temperature for 2.5 h. Then 100 mL of water was added and the mixture extracted with ether. The combined organic layers were washed with water and sodium carbonate solution and then dried over magnesium sulfate. Evaporation of the solvent gave 5.2 g of viscous red oil, which was chromatographed with 3:1 petroleum ether–ethyl acetate to give 1.14 g (2.16 mmol, 25% yield) of 6. Two recrystallizations from chloroform–ethanol–water gave yellow needles: mp 227–228 °C dec; IR (KBr) 3600–3200 (OH), 1500 (NO$_2$) cm^{-1}; ^{1}H NMR (acetone-d_6, 90 MHz) δ 7.95 (d, J = 9 Hz, 2 H, H-4,4′), 7.22 (d, 2 H, H-3,3′); mass spectrum, m/z 401 (M$^+$ − I).

Anal. Calcd for $C_{12}H_6O_6N_2I_2$: C, 27.30; H, 1.15; N, 5.31; I, 48.07. Found: C, 27.58; H, 1.41; N, 5.31; I, 46.71.

Also obtained in the preceding chromatographic separation was 0.89 g (20%) of 6,6′-diiodo-3,5′-dinitro-2,2′-biphenyldiol: ^{1}H NMR (acetone-d_6, 90 MHz) δ 8.11–7.98 (m, 2 H, H-4, H-4′), 7.79 (d, J = 9 Hz, 1 H, H-5), 7.22 (d, J = 9 Hz, 1 H, H-3′).

2,2′-Bis(benzyloxy)-6,6′-diiodo-5,5′-dinitrobiphenyl (7). A mixture of 0.92 g (1.75 mmol) of 6, 0.53 g of anhydrous potassium carbonate, 0.63 g (3.67 mmol) of benzyl bromide, 10 mL of 1,2-dimethoxyethane, and 3 mL of dimethylformamide was heated at 60–70 °C for 1 h under argon. The solvent was removed at reduced pressure, water was added, and the mixture was extracted with chloroform. The extract was dried with magnesium sulfate and the solvent removed to give 2.04 g of reddish oil. The oil was chromatographed with 7:1 petroleum ether–ethyl acetate to give 0.68 g (0.96 mmol, 55% yield) of yellow crystalline 7. Three recrystallizations from ethanol gave yellow needles: mp 196–197.3 °C; IR (KBr) 1560, 1330 (NO$_2$) cm^{-1}; ^{1}H NMR (acetone-d_6, 60 MHz) δ 8.03 (d, J = 8 Hz, 2 H, H-4,4′), 7.42–7.22 (m, 12 H, H-3,3′, C$_6$H$_5$), 5.23 (s, 4 H, CH$_2$); mass spectrum, m/z 581 (M$^+$ − I).

Anal. Calcd for $C_{26}H_{18}O_6N_2I_2$: C, 44.09; H, 2.56; N, 3.96; I, 35.84. Found: C, 44.27; H, 2.56; N, 3.93; I, 35.20.

Table I. Acidity Constants and Extinction Coefficients of 4,5-Dinitro-1,8-biphenylenediol[a]

	260 nm	297 nm	343 nm	355 nm	373 nm
ϵ_{H_2A}, M^{-1} cm^{-1}	9010	16670	7820	5990	3080
	(70)	(100)	(30)	(30)	(30)
ϵ_{HA}, M^{-1} cm^{-1}	14650	11030	13780	11360	8830
	(160)	(120)	(90)	(100)	(120)
ϵ_A, M^{-1} cm^{-1}	20020	7940	17590	17220	13560
	(180)	(70)	(100)	(130)	(180)
10^6K_1, M	3.6	2.7	2.5	2.4	2.3
	(0.4)	(0.3)	(0.1)	(0.2)	(0.2)
10^9K_2, M	4.5	3.3	2.6	2.8	2.6
	(0.9)	(0.6)	(0.4)	(0.3)	(0.5)

[a] In water at 26 °C. The parenthesized figures are estimated standard deviations.

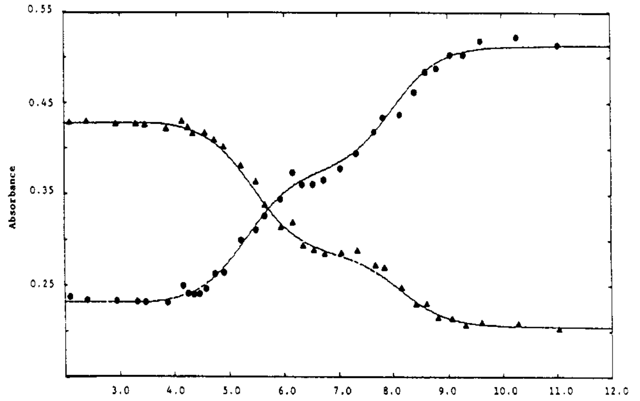

Figure 1. Plots of absorbances of 2.568 × 10^{-6} M 4,5-dinitro-1,8-biphenylenediol in 10-cm cells vs. pH in water at 26 °C: (■) at 260 nm; (▲) at 297 nm. The lines are plots of values calculated from the ionization constants and extinction coefficients shown in Table I.

1,8-Bis(benzyloxy)-4,5-dinitrobiphenylene (8). A mixture of 1.77 g (2.5 mmol) of 7, 2.0 g of activated copper bronze,[6] and 25 mL of dimethylformamide was refluxed for 4 h under argon. The cooled mixture was poured into 50 mL of water at 0 °C and filtered. The solid was extracted in a Soxhlet extractor will acetone for 24 h and with methylene chloride for 48 h. Removal of the solvents from the extract gave 2.0 g of brown solid, which was recrystallized from chloroform–hexane to give 480 mg (1.06 mmol, 42% yield) of orange crystals. Two recrystallizations more from chloroform–hexane gave 8: mp 218–218.8 °C; IR (KBr) 1510, 1355 (NO$_2$) cm^{-1}; ^{1}H NMR (CDCl$_3$, 200 MHz) δ 7.247–7.196 (m, 12 H, H-3,6, C$_6$H$_5$), 6.714 (d, J = 9.52, 2 H, H-2,7), 5.089 (s, 4 H, CH$_2$); mass spectrum, m/z 454 (M$^+$).

Anal. Calcd for $C_{26}H_{18}O_6N_2$: C, 68.72; H, 3.99; N, 6.16. Found: C, 68.80; H, 4.15; N, 6.04.

4,5-Dinitro-1,8-biphenylenediol (1). To a suspension of 98 mg (0.22 mmol) of 8 in 15 mL of benzene was added 0.86 mL of 1 M boron tribromide in hexane at room temperature under argon. After the mixture had been stirred at room temperature for 3.5 h, 15 mL of 0 °C water was added in an ice bath. The mixture was then extracted with ether and the ether evaporated from the extract. The resulting orange solid was an almost quantitative yield of 1 (one spot on thin layer chromatography using silica gel, R_f 0.24 with 1:1 acetone–petroleum ether). Two recrystallizations from 95% ethanol–chloroform gave orange needles: mp 274–276 °C dec; IR (KBr) 3600–3200 (OH), 1500, 1345 (NO$_2$) cm^{-1}; ^{1}H NMR (methanol-d_4, 200 MHz) δ 6.993 (d, J = 9.4 Hz, 2 H, H-3,6), 6.405 (d, 2 H, H-2,7); mass spectrum, m/z 274 (M$^+$).

Anal. Calcd for $C_{12}H_6O_6N_2$: C, 52.57; H, 2.21; N, 10.22. Found: C, 52.01; H, 2.25; N, 9.94.

Acidity Constants. The acidity constants of 4,5-dinitro-1,8-biphenylenediol in water at 26 °C were determined by measuring its apparent extinction coefficient at 260, 297, 343, 355, and 373 nm at a number of pH values as described previously for 1,8-biphenylenediol.[9] The ionic strengths of the solutions

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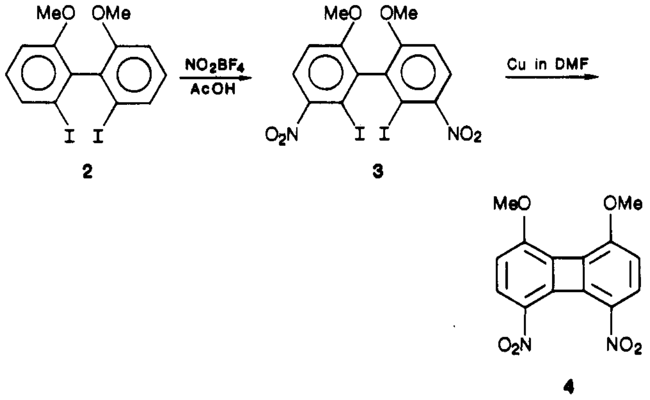
used ranged from 0.001 to 0.165. The results are summarized in Table I and the data obtained at 260 and 297 nm are plotted in Figure 1. The theoretical lines are based on an average ionic strength of 0.100. The average thermodynamic pK values (standard deviations) were pK_1 5.60 (0.09) and pK_2 8.54 (0.13).

Results and Discussion

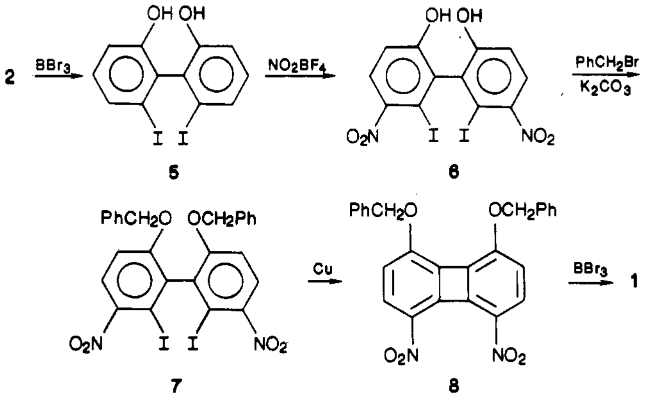
Synthesis. We first tried to prepare 1 from the readily available 2,3-dichloroanisole. Nitration gave the desired 2,3-dichloro-4-nitroanisole in 17–25% yield, but attempted transformation of this to 4,5-dinitro-1,8-dimethoxybiphenylene (4) by reaction with activated copper bronze in refluxing dimethylformamide was unsuccessful, with the only identified product being 2-chloro-4-nitroanisole.

A second attempt started with 2,2′-diiodo-6,6′-dimethoxybiphenyl (2), already in hand as an intermediate in the synthesis of 1,8-biphenylenediol.[8,9] Nitration of 2 gave the desired 2,2′-diiodo-6,6′-dimethoxy-3,3′-dinitrobiphenyl (3) in up to 48% yield along with the 3-nitro, 5-nitro, 3,5′-dinitro, and 3,3′,5,5′-tetranitro derivatives. Reaction of 3 with copper bronze in refluxing dimethylformamide gave 79% 4. However, all the many methods used in attempting to demethylate 4 were unsuccessful. These include the use of boron tribromide, with[10] and without dimethyl sulfide, aluminum chloride, and aluminum bromide with dimethyl sulfide and/or ethanethiol,[11] trimethylsilyl iodide in acetonitrile and in dimethyl sulfoxide,[12] boiling 48% hydrobromic acid in the presence of a phase transfer catalyst,[13] pyridine with and without[14] added 4-(dimethylamino)pyridine, and sodium thioethoxide, potassium *tert*-butoxide, and sodium iodide, all in dimethylformamide.



The method finally used for the synthesis of 1 started with the demethylation of 2 to 6,6′-diiodo-2,2′-biphenyldiol (5), which was then nitrated to give 25–28% 6,6′-diiodo-5,5′-dinitro-2,2′-biphenyldiol (6) and about 20% 6,6′-diiodo-3,5′-dinitro-2,2′-biphenyldiol. Benzylation of 6 using benzyl bromide and potassium carbonate[15] gave 55–60% 2,2′-bis(benzyloxy)-6,6′-diiodo-5,5′-dinitrobiphenyl (7) and an unidentified byproduct. Ring closure in 7 was achieved by use of copper bronze to give 42–45% 1,8-bis(benzyloxy)-4,5-dinitrobiphenylene (8). Debenzylation of 8 gave 1 in almost quantitative yield.

Acidity Constants. The para nitro substituent plus the other nitro substituent, also separated by four carbons from the acidic hydroxy group, decrease the pK_1 value of 1 by 2.41 units relative to that of the unnitrated compound.[9] This is less than the 2.83 unit increase in acidity produced by one para nitro group in phenol or the 3.61 unit increase produced in α-naphthol.[16,17] This greatly reduced electron withdrawing power of the nitro substituent in the biphenylene ring could be blamed on the reluctance of the four-membered ring to contain two (antiaromatic) double bonds, which is reflected in the marked tendency of the bond lengths to alternate in the "benzene" rings of biphenylene derivatives, with longer bonds falling in the four-membered rings.[18,19] This should decrease the contribution of a quinoid structure to the resonance hybrid structure of the monoanion of 1. Since the diquinoid structure for the dianion of 1 would contain a cyclobutadiene ring, pK_2 should be affected even more than pK_1. In fact, however, the difference between pK_1 and pK_2 (2.94) for 1 is essentially the same as for the unnitrated compound (2.99).[9] The most plausible explanation for the facts is steric inhibition of resonance. The two nitro groups would crowd each other excessively if they were both coplanar with the biphenylene ring. In fact, in the double hydrogen bonded adduct of 1 with 2,6-dimethyl-γ-pyrone the nitro groups are at dihedral angles of 20° and 43° [20]



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Basicity of, S_N2 Reactivity of, and Basic Catalysis by 1-Azabicyclo[2.2.1]heptane[1]

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Relatively unhindered tertiary amines have been found to be particularly rapid reactants in a number of reactions. In the dedeuteriation of isobutyraldehyde-*2-d*, for example, a Brønsted plot showed that the best basic catalysts, for their basicity, are trimethylamine and 1,4-diazabicyclo[2.2.2]octane,[2] which are several times as reactive as me-

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